

## **APPENDIX A**

### **FIELD INVESTIGATION METHODOLOGIES**

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## **SECTION A-1**

### **INTRODUCTION**

Detailed site characterization is an important aspect of the remediation by monitored natural attenuation. Typically, it is necessary to collect additional site-specific data in order to successfully complete the demonstration. This appendix presents an overview of field techniques that can be used to collect the data used to evaluate monitored natural attenuation. These techniques are most appropriate for aquifers in unconsolidated sediments. They are less appropriate for fractured rock, and karst hydrogeologic settings. Selection of locations for field investigation activities and analytical protocols used for soil and water samples are discussed in Section 2 of the protocol document.

During all field investigation activities, special care should be taken to prevent contamination of the sampled matrices. The primary way that sample contamination can occur is through contact with improperly cleaned equipment. To prevent such contamination, proper equipment decontamination procedures must be developed and followed. Procedures will vary according to site contaminants, equipment type, field activity, sample matrix, rinseate handling requirements, and regulatory requirements. All equipment requires decontamination prior to initiation of site activities and between sampling locations. New, disposable equipment does not require decontamination if factory-sealed and found acceptable according to the appropriate data quality objectives and the site specific Quality Assurance Plan. In addition to the use of properly cleaned equipment, new, clean, disposable gloves (of a material appropriate to the activity and contaminant type/concentration) should be worn at each new sampling location.

Basic health and safety precautions are required for every piece of equipment and every methodology discussed in this section. It is the responsibility of the investigator to be aware of and to communicate all health and safety issues to the field team; therefore, a site specific health and safety plan must be developed prior to initiating investigation activities. At a minimum this plan must contain:

- A safety and health risk analysis for chemical, physical, and biological hazards associated with the site conditions, anticipated contaminants, equipment, field activities, and climate;
- An emergency response plan with applicable emergency response numbers; and
- Precautionary measures to be implemented to insure the safety of site workers.

This appendix consists of seven sections, including this introduction. Section A-2 discusses subsurface investigation methodologies. Section A-3 discusses soil characterization methodologies. Section A-4 discusses groundwater characterization methodologies. Section A-5 discusses surface water and sediment characterization methodologies. Section A-6 discusses sample handling procedures. Section A-7 discusses aquifer characterization methodologies.

## **SECTION A-2**

### **SUBSURFACE INVESTIGATION METHODOLOGIES**

The ideal technologies for an investigation of monitored natural attenuation are those which can rapidly provide a large amount of information in a very short period of time while producing low quantities of waste. The following subsections briefly introduce several alternatives that are available for performing subsurface investigations to evaluate remediation by monitored natural attenuation. Although some of these alternatives more closely achieve the objectives of remediation by monitored natural attenuation investigation than others, considerations such as site geology, site hydrogeology, future well use, or regulatory concerns may dictate the selection of the subsurface investigation method for any given site. It is crucial to the evaluation of monitored natural attenuation to consider all of these issues prior to selecting a technology appropriate for their site. If during the investigation it becomes necessary to change methodologies, the same concerns must be re-addressed.

Prior to initiating any intrusive subsurface activities, proposed drilling locations must be cleared. It is particularly useful if all utility lines in the investigation area are marked should changes to the investigation become necessary. In addition, in order to expedite the investigation, all necessary digging, coring, drilling, and ground-water monitoring point installation permits should be obtained prior to mobilizing to the field. Care should be taken not to cross-contaminate deeper aquifers by drilling through an aquitard underlying a DNAPL.

At the conclusion of subsurface investigations, each sampling location that is not used to install a ground-water monitoring point or well should be restored as closely to its original condition as possible. Where possible, holes should be sealed with bentonite chips, pellets, or grout to eliminate any creation or enhancement of contaminant migration pathways to the ground water.

#### **A.2.1 TRADITIONAL DRILLING TECHNIQUES**

Traditional drilling techniques include those methods that traditionally have been used to install drinking water supply wells. Examples of traditional drilling techniques include hollow stem auger, rotary, air percussion, and cable tool or chain tool. They have in common the advantage of being capable of installing wells of varying diameters to drinking water well specifications. Each of these techniques also allows for visual description of the materials and can allow for easy stratigraphic correlation. In general, the equipment required by each of these techniques is readily available. Disadvantages of traditional drilling techniques include their expense, time requirements, and waste generation. Not only do these techniques produce soil/fluids from the drilling process, frequently, in order to properly develop wells by these techniques, a large volume of ground water must be extracted during a lengthy development. Although the advantages and disadvantages listed above are common to most traditional drilling techniques, they are applicable to varying degrees. Furthermore, drilling depth and subsurface stratigraphy are important considerations when evaluating the efficacy of each of these techniques.

Hollow-stem auger has been the most widely used traditional drilling technique in environmental investigations, because it is very effective in the most commonly investigated geologic setting encountered during environmental investigations: unconsolidated deposits at shallow depths. Although less common, a chain tool can also be effective under similar geologic conditions. When installing wells, a chain tool may require a little more time, but may prove to be less disruptive to the formation in the vicinity of the well screen. Both techniques are well suited to collecting continuous soil samples using a split-barrel continuous sampling device. This capability is extremely important because detailed knowledge of the subsurface can be critical to the successful demonstration of remediation by monitored natural attenuation.

At greater depths and in more competent formations, rotary and air hammer techniques are frequently used. Rotary techniques are also suited to penetration of cobbly units that may prove difficult or impenetrable to a hollow-stem auger or chain tool. With rotary rigs, the fastest drilling rates are usually achieved by using drilling fluids such as mud or water; however, these fluids may require handling as IDW and may clog the pore space in the vicinity of the well screen. As long as air circulation can be maintained in the borehole, an air hammer can be particularly useful in competent bedrock formations without introducing drilling fluids.

### **A.2.2 CONE PENETROMETER TESTING**

CPT is increasingly being used for successful site characterization. CPT is accomplished using a cone penetrometer truck, which consists of an instrumented probe that is forced into the ground using a hydraulic load frame mounted on a heavy truck, with the weight of the truck providing the necessary force. Penetration force is typically supplied by a pair of large hydraulic cylinders bolted to the truck frame. In tight soils, push capacity is more often limited by the structural bending capacity of the push rods than by the weight of the truck. Cone penetrometers operate well in most unconsolidated deposits; however, they may not be able to penetrate and may be damaged by cobbles, gravel layers, very stiff clays, and cemented units.

The penetrometer probe generally consists of a 60-degree conical tip attached to a friction sleeve. Inside the probe, two load cells independently measure the vertical resistance against the conical tip and the side friction along the sleeve. Each load cell is a cylinder of uniform cross section inside the probe which is instrumented with four strain gauges in a full-bridge circuit. Forces are sensed by the load cells, and the data are transmitted from the probe assembly via a cable running through the push tubes. The analog data are digitized, recorded, and plotted by computer in the penetrometer truck. Penetration, dissipation, and resistivity data are used to determine site stratigraphy.

The cone penetrometer can be a very effective tool for collecting large quantities of subsurface information in a short period of time with virtually no waste generation. A cone penetrometer also can be used for installation of ground-water monitoring points, and specially equipped penetrometers can be used to screen for mobile and residual fuel hydrocarbon contamination using laser induced fluorescence (LIF). Although the equipment is fairly expensive, the overall efficiency can make this option relatively inexpensive.

Most of the disadvantages of CPT are linked to the advantages. For instance, the speed and minimal waste associated with CPT are directly related to the process of determining lithology in situ; however, this does not allow for visual description of subsurface materials. Isolated soil samples can be retrieved for visual description to calibrate the cone penetrometry log, but the procedure cannot be performed frequently (nor continuously) without impairing the efficiency of the penetrometer. And while CPT can be very effective at precisely determining changes in lithology on the basis of grain size, the lack of a visual description prevents stratigraphic correlation on the basis of other parameters, such as color. The U.S. DoD supports a technology development program for site characterization using cone penetrometers (the SCAPS program). SCAPS has developed a down-hole CCD camera and light source that can visualize subsurface sediments.

Monitoring points installed using a cone penetrometer illustrate another advantage that comes with disadvantages. CPT allows for rapid placement of discreet ground-water sampling points at a precise depth selected on the basis of real-time, detailed, stratigraphic logs. The most effective emplacement technique allows for installation of monitoring points of not greater than approximately 0.5 inch ID. While these points may not require much development or purging, ground-water extraction for development, purging, and sampling becomes extremely inefficient if the depth to ground

water is greater than approximately 25 feet. In addition, the monitoring point emplacement technique typically does not allow for installation of a sand pack, bentonite seal, and grout slurry as may be required by regulations.

### **A.2.3 HYDRAULIC PERCUSSION SYSTEMS**

A variety of sampling tools can be advanced through unconsolidated soils using relatively inexpensive hydraulically powered percussion/probing machines (e.g., Geoprobe®). These sorts of systems are frequently mounted on pickup trucks or all-terrain vehicles and, as a result of their small size and versatility, can access many locations that larger equipment cannot.

Hydraulic percussion systems provide for the rapid collection of soil, soil gas, and ground-water samples at shallow depths while minimizing the generation of investigation-derived waste materials. Specifically undisturbed, continuous soils samples can rapidly be collected for visual observation, field analysis, and/or laboratory analysis. In addition, ground-water samples can be collected through the probe rods, or ground-water monitoring points can be installed for later sample collection. Although monitoring points installed by hydraulic percussion systems can vary considerably in design and can include sandpicks and seals, monitoring points are typically narrow in diameter. As a result, it can be difficult to sample points where the ground-water elevation is greater than 25 feet bgs. Furthermore, the narrow diameter may not comply with regulatory standards or future use needs.

## **SECTION A-3**

### **SOIL CHARACTERIZATION METHODOLOGIES**

As part of an evaluation of monitored natural attenuation for contaminants in ground water, soil characterization factors into development of a site conceptual model, estimation of continuing source strength, and modeling of fate and transport. The following sections describe soil sample acquisition, description, field screening, and laboratory analysis procedures. Samples should be collected in accordance with local, State, and Federal requirements.

#### **A.3.1 SAMPLE ACQUISITION**

Soil samples can be collected using a variety of methods, depending upon the method used to advance boreholes. In all cases, the goal is to collect samples to allow lithologic logging and to provide useable samples for field screening and for submission to an analytical laboratory. The samples should meet the appropriate data quality objectives as identified in the site-specific Quality Assurance Plan.

When using hollow-stem auger or chain tool methods, relatively undisturbed continuous soil samples can be collected with split-barrel samplers that are either advanced using a hydraulic hammer or are driven along with the advancing auger. These are well-tested methods that are useful in most types of soils except for saturated sands, in which samples tend to liquify and slide out of the barrel. Collection of continuous samples allows a more thorough description of site geology, with only a slight increase in the time required for drilling. These methods also can be used to collect samples in various types of liners, such as acetate or brass sleeves. These sleeves can be cut, capped, and shipped with a minimum of effort. When using sleeves, the samples are disturbed less, but description of the soils may be hindered if the liners are not clear. Other traditional drilling methods (i.e., rotary) do not produce samples that can be used for chemical analysis, and will also make geologic interpretation more difficult due to the disturbed nature of the material.

If CPT or hydraulic percussion methods are used, soil sampled can be collected using a hydraulically driven sampler. When soil samples are collected using a probe-drive sampler, the probe-drive sampler serves as both the driving point and the sample collection device and is attached to the leading end of the driving rods. To collect a soil sample, the sampler is pushed or driven to the desired sampling depth, the drive point is retracted to open the sampling barrel, and the sampler is subsequently pushed into the undisturbed soils. The soil cores are retained within brass, stainless steel, or clear acetate liners inside the sampling barrel. The probe rods are then retracted, bringing the sampling device to the surface. The soil sample can then be extruded from the liners for lithologic logging, or the liners can be capped and undisturbed samples submitted to the analytical laboratory for testing.

If a hand auger is used, samples will be slightly disturbed, but still useful for logging purposes. Removing soil from the auger bucket may prove difficult where soils are clayey. Below the water table, it may be impossible to retain sandy soils in the bucket. Hand driven samplers are similar to probe-drive samplers, except that all pushing power is provided manually.

Following sample acquisition, the coordinates and elevation of all soil sampling locations should be surveyed. Horizontal coordinates should be measured to the nearest 0.1 foot relative to an established coordinate system, such as state planar. The elevation of the ground surface also should be measured to the nearest 0.1 foot relative to USGS mean sea level (msl) data.

#### **A.3.2 PHYSICAL DESCRIPTION**

Physical characterization of soils should be performed at all sampling locations and a descriptive log prepared for the materials encountered. If using CPT, the descriptive logs should consist of continuous computer-generated interpretations supplemented by periodic sensory confirmation and

description. Otherwise, continuous sampling with interpretation and description is recommended in order to precisely identify and isolate changes in lithology. The descriptive log should contain:

- Sample interval (top and bottom depth);
- Sample recovery;
- Presence or absence of contamination;
- Lithologic description, including relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations; and
- Depths of lithologic contacts and/or significant textural changes measured and recorded to the nearest 0.1 foot.

In addition, representative samples should be photographed, labeled, and stored. Additional site characterization features are frequently being added to the list of desirable parameters. Static pore pressure and transient pore pressures during penetration with a cone penetrometer are examples.

### **A.3.3 FIXED-BASE LABORATORY ANALYSES**

Portions of selected samples should be sent to the fixed-base laboratory for analysis. It is desirable to sample and submit a relatively undisturbed sample, if possible. Undisturbed samples are typically collected in brass, stainless steel, or clear acetate liners inside of a sampling barrel. Upon removal from the barrel, liners are cut to length (if desired) and capped. If the selected drilling technique, site conditions, or project requirements do not permit collection of undisturbed soils, samples for analysis of volatile constituents should be transferred immediately to an appropriate container in such a way as to minimize volatilization during the transfer and headspace in the sample container. The analytical protocol to be used for soil sample analysis is presented in Table 2.1. This analytical protocol includes the parameters necessary to document the effects of sorption and to estimate the magnitude of the continuing source. The protocol document describes each soil analytical parameter and the use of each analyte in the demonstration of remediation by monitored natural attenuation.

Each laboratory soil sample will be placed in an analyte-appropriate sample container and delivered as soon as possible to the analytical laboratory for analysis of total hydrocarbons, aromatic hydrocarbons, VOCs, and moisture content using the procedures presented in Table 2.1. In addition, at least two samples from locations upgradient, crossgradient, or far downgradient of the contaminant source will be analyzed for TOC, and the chemical and geochemical parameters necessary to characterize the processes and rates of reaction occurring within the plume.

## **SECTION A-4**

### **GROUND-WATER CHARACTERIZATION METHODOLOGIES**

This section describes the scope of work required to collect ground-water quality samples and to perform field analyses to evaluate the demonstration of remediation by monitored natural attenuation. Ground-water sampling should be conducted only by qualified scientists and technicians trained in the conduct of well sampling, sampling documentation, and chain-of-custody procedures. In addition, sampling personnel should thoroughly review this protocol document and the site-specific work plan and quality assurance plan prior to sample acquisition and have a copy of the work plan and quality assurance plan available onsite for reference. Samples should be collected in accordance with local, State, and Federal requirements.

#### **A.4.1 GROUND-WATER MONITORING LOCATIONS, DEPTHS, AND SCREENED INTERVALS**

Ground-water monitoring locations should be selected on the basis of the preliminary conceptual site model and information on the three-dimensional distribution of contaminants. At a minimum, one monitoring location should be placed upgradient from the contaminant plume, one location should be placed in the suspected source area, two locations should be placed within the plume, and three locations should be placed various distances downgradient and crossgradient from the plume. The actual number of monitoring locations could be considerably higher and should be related to site conditions and the size of the source.

It is necessary to collect samples that document the vertical extent of contamination at several or at all of the ground-water monitoring locations. This decision is based on the presence of confining units, the thickness of the aquifer, the type and source of contamination, and suspected variations in subsurface transmissivity. The position of well screens should be selected by the field scientist after consideration is given to the geometry and hydraulic characteristics of the stratum in which the well will be screened. Wells should be screened so that the vertical distribution of contaminants and hydraulic gradients can be delineated. Typically the shallowest ground-water monitoring depth is chosen to intersect the water table. This allows for the monitoring of LNAPL and seasonal water level fluctuations, as well as dissolved contaminant concentrations in the portion of the aquifer closest to the typical source. Deeper locations are selected on the basis of contaminant distribution, typically above or below suspected confining units or in zones believed to possess higher transmissivity. To ensure well integrity, clustered monitoring wells/monitoring points generally should be completed in separate boreholes.

Screen lengths of not more than 5 feet are recommended to help mitigate the dilution of water samples from potential vertical mixing of contaminated and uncontaminated ground water. Screening a larger area of the saturated zone will result in averaging of contaminant concentrations and hydraulic properties. In addition, short screened intervals used in nested pairs give important information on the nature of vertical hydraulic gradients in the area.

#### **A.4.2 TYPES OF GROUND-WATER SAMPLING LOCATIONS**

Ground-water samples for the demonstration of remediation by monitored natural attenuation can be collected from monitoring wells, monitoring points, or grab sampling locations. Monitoring points and grab locations provide rapid and inexpensive access to shallow ground-water, and yield ground-water samples that are appropriate for site characterization and plume definition. Conventional monitoring wells are required for sites with ground-water elevations more than approximately 25 feet below ground surface. They also are recommended for long-term monitoring (LTM) and performance evaluation ground-water sampling, and may be required for regulatory compliance.

Following installation, the location and elevation of all ground-water monitoring locations should be surveyed. Horizontal coordinates should be measured to the nearest 0.1 foot relative to an

established coordinate system, such as state planar. The elevation of the ground surface also should be measured to the nearest 0.1 foot relative to USGS mean sea level (msl) data. Other elevations, including the measuring point, should be measured to the nearest 0.01 foot.

#### **A.4.2.1 Monitoring Wells**

Monitoring wells are commonly installed to evaluate remediation by monitored natural attenuation. As used in this document, monitoring wells are assumed to have, at a minimum, a sand pack, a bentonite seal, an annular seal, a surface seal, and an inside diameter of at least 2 inches. Monitoring wells are extremely versatile and can be used for ground-water sampling, aquifer testing, product recovery systems, long-term monitoring, and performance evaluation monitoring. Although versatile, monitoring wells are relatively expensive to install and create relatively large quantities of waste during installation, development, and sampling. Detailed well installation procedures are described in the following paragraphs. Of course, local protocols, regulations, type of drill rig, site conditions and site-specific data uses should dictate actual well completion details.

The monitoring well should be installed in a bore hole with a diameter at least 4 inches larger than the outside diameter of the well. At a minimum, blank well casing and screen should be constructed of Schedule 40 polyvinyl chloride (PVC) with an inside diameter (ID) of 2 inches. Frequently, this diameter must be increased if the well may be used for a pumping test or certain types of product or ground-water recovery. The screens should be factory slotted with appropriately sized openings (typically 0.010-inch). All well sections should be flush-threaded; glued joints should not be used. The casing at each well should be fitted with a threaded bottom plug and a top cap constructed of the same type of material as the well casing. The top should be vented to maintain ambient atmospheric pressure within the well casing. It is possible that PVC will not be suitable for use in wells intended to monitor high concentrations of volatile organic constituents.

Once the well is in place, sand, bentonite, and grout are used to fill the remaining borehole annulus. Appropriately-sized sand must be packed along the entire length of the screen; however, it is desirable to limit the vertical distance that the sand pack extends to either side of the screen (i.e., at least 6 inches but less than 2 feet) because the added sand pack can increase the portion of the aquifer that is effectively screened. A bentonite seal is placed on top of the sand pack. If conditions permit, this seal should have a minimum thickness of 2 feet. A cement-bentonite grout is used to fill the remainder of the annular space between the bentonite seal and the surface completion. Depending on site conditions and facility preferences, either flush-mount or stick-up surface completions can be used. Site conditions and local, State, and Federal requirements should ultimately dictate materials selection and construction details.

The field scientist should verify and record the boring depth, the lengths of all casing and screen sections, and the depth to the top of all well completion materials placed in the annulus between the casing and borehole wall. All lengths and depths should be measured to the nearest 0.1 foot.

#### **A.4.2.2 Monitoring Points**

Where site conditions and the regulatory environment permit, monitoring points are ideal tools for rapidly and cost-effectively obtaining site data to evaluate a remediation by monitored natural attenuation. Monitoring points can be installed and sampled rapidly while generating a minimal volume of waste. Furthermore, some monitoring points cannot be used for ground-water or free product level measurements. It is always useful when a site has a reasonable and adequate number of monitoring wells. Detailed monitoring point installation procedures are described in the following paragraphs. Of course, local protocols, regulations, available equipment, and site conditions should dictate actual well completion details.

In this document, monitoring points are considered temporary or permanent ground-water sampling locations that do not meet the specifications of monitoring wells. Typically monitoring

points are installed in small diameter boreholes using CPT, hydraulic percussion, or manually-powered equipment. As a result, monitoring points usually have an ID of less than 2 inches. In addition, because of the extremely small to nonexistent annular space between the borehole wall and the monitoring point materials, they seldom have a sand pack, bentonite seal, and grout seal, particularly with an annulus of 2 inches. Because these components are missing, ground-water monitoring points should be installed only in shallow aquifers where installation of such devices will not result in the cross-contamination of adjacent water-bearing strata.

Like monitoring wells, monitoring points are typically constructed of Schedule 40 PVC casing and screen; however, monitoring points also can be constructed from Teflon®-lined tubing attached to a stainless steel, wire mesh screen. Because the screens are often installed without a sand pack, a slot size of 0.010 inch or smaller should be used. All monitoring point casing and screen sections should be flush-threaded; glued joints should not be used. The casing at each monitoring point should be fitted with a bottom cap and a top cap constructed of PVC. The top cap should be vented to maintain ambient atmospheric pressure within the monitoring point casing. Site conditions and local, State, and Federal requirements should ultimately dictate materials selection and construction details.

The field hydrogeologist should verify and record the total depth of the monitoring point, the lengths of all casing and screen sections, and the depth to the top of all monitoring point completion materials. All lengths and depths should be measured to the nearest 0.1 foot.

#### **A.4.2.3 Grab Sampling**

Ground-water grab samples are temporally and spatially discrete samples collected from boreholes that are abandoned upon completion of sampling. In highly transmissive aquifers, the collection of grab samples can provide a rapid, cost-effective alternative to the use of monitoring points. Like monitoring points, collection of grab samples generates minimal waste; however, they are not appropriate for aquifer testing, remediation systems, or long-term monitoring. Furthermore, because the locations are abandoned upon completion of sampling, analytical results cannot be confirmed, and ground-water levels at all locations cannot be collected over the space of a few hours for use in the development of ground-water flow maps. In addition, if the aquifer is not particularly transmissive, sample collection can require hours resulting in inefficient equipment utilization. For these reasons, installation and sampling of monitoring points typically is recommended where feasible. Several of the more common instruments used to collect ground-water grab samples include the HydroPunch®, Geoprobe®, cone penetrometer, or hand-driven points. An optimal site characterization approach often involves use of grab samples acquired by push technologies such as the HydroPunch®, Geoprobe®, cone penetrometer, or hand-driven points for a rapid, three-dimensional characterization of the site, then using that information to select locations and screened intervals for permanent monitoring points.

### **A.4.3 MEASUREMENT OF STATIC FLUID LEVELS**

#### **A.4.3.1 Water Level and Total Depth Measurements**

Prior to purging or developing any water from a ground-water sampling location, the static water level should be measured. At all locations of sufficient diameter, an electric water level probe should be used to measure the depth to ground water below the datum to the nearest 0.01 foot. Small diameter probes are commercially available for measurement of water levels in monitoring points and through Geoprobe®, HydroPunch®, and CPT pushrods. After measuring the static water level, the water level probe should be slowly lowered to the bottom of the well, and the total well depth should be measured to the nearest 0.01 foot. If measuring from the ground surface, an accuracy better than 0.1 foot is probably not practical. Based on these measurements the volume of water to be developed or purged from the location can be calculated. If mobile LNAPL is encountered, the

LNAPL thickness should be determined, and attempts should be made to sample both the ground water below the LNAPL layer as well as the LNAPL.

If a sufficiently narrow water level probe is unavailable, hollow, high-density polyethylene (HDPE) tubing connected to a manometer can be used to determine depth to ground water. The manometer will indicate when ground water is reached as the HDPE tubing is inserted into the monitoring location. The HDPE attached to the manometer will then be marked at the level of the ground surface and removed. The depth to water will be determined by placing a tape measure next to the HDPE tubing and measuring the length from the base of the tubing to the ground level mark to the nearest 0.01 foot, if possible.

#### **A.4.3.2 Mobile LNAPL Thickness Measurements**

At sites where phase-separated hydrocarbons are present in the ground-water system, it is important to accurately measure the thickness of floating hydrocarbons. Accurate measurement of hydrocarbon thickness allows for estimation of the amount and distribution of the hydrocarbon and correction of measured ground-water elevations. There are three methods that can be used to determine the thickness of mobile LNAPL in a well, including use of an interface probe, a bailer, or tape and paste. Interface probes generally operate on either light refraction sensors or density float switches to detect hydrocarbons and the hydrocarbon/water interface. The depth to mobile LNAPL and depth to water should be measured to the nearest 0.01 foot. The thickness of phase-separated hydrocarbons should also be measured to the nearest 0.01 foot. Three consecutive measurements should be made to ensure the accuracy of the measuring instrument. A clear bailer can be slowly lowered into the well until it intersects the fluid but is not totally immersed. The bailer is then retrieved, and the floating LNAPL can be visually observed and measured with an engineer's tape. The third method for measurement of floating hydrocarbon thickness is hydrocarbon paste and an engineer's tape. The paste, when applied to the tape, changes color when it intersects the hydrocarbon and the hydrocarbon/water interface. Measurements of the mobile LNAPL thickness can be made directly from the engineer's tape. It is extremely important to remember to thoroughly decontaminate all equipment between well measurement events to prevent cross-contamination of wells. Equipment blanks, part of the Quality Assurance Program, will confirm the suitability of the decontamination activities.

Measurements of mobile LNAPL thickness made in monitoring wells provide only an estimate of the actual thickness of NAPL at that location. Actual mobile and residual LNAPL thicknesses can only be obtained from continuous soil cores. Correcting apparent mobile LNAPL thickness as measured in monitoring wells to true thickness is discussed in Appendix C.

#### **A.4.3.3 Mobile DNAPL Thickness Measurements**

DNAPL thickness in wells cannot be used to estimate actual DNAPL quantities on a site.

### **A.4.3 GROUND-WATER EXTRACTION**

Varied equipment and methods are available for the extraction of ground water. The approach is determined on the basis of application (development, purging, or sampling), hydrogeologic conditions, monitoring location dimensions, and regulatory requirements.

Ground water produced during extraction activities must be handled in a manner consistent with the investigation-derived waste (IDW) plan for the site. The method of handling and disposal will depend on location and type of source, site contaminants, degree of contamination (e.g., free product, odor, air monitoring measurements), and applicable local, State, and Federal regulations.

#### **A.4.3.1 Methods**

Portable ground-water extraction devices from three generic classifications are commonly used for investigations of monitored natural attenuation: grab, suction lift, and positive displacement.

The selection of the type of device(s) for the investigation is based on type of activity, well/point dimensions, and hydrogeologic conditions.

Bailers are common grab sampling devices. Disposable bailers can be used to avoid decontamination expenses and potential cross-contamination problems. Drawbacks for bailers include agitation/aeration of the ground water and the inability to maintain a steady, non-turbulent flow required to establish a true flow-through cell. Aeration also can be an issue during transfer of the sample from the bailer to the sample container. As a result of aeration, and because a true flow-through cell cannot be established, accurate dissolved oxygen and ORP measurements can be difficult to obtain.

The suction lift technology is best represented in environmental investigations by the peristaltic pump. A peristaltic pump extracts water using a vacuum created by cyclically advancing a sealed compression along flexible tubing. This pumping technique means that extracted water contacts nothing other than tubing that can be easily replaced between sampling locations. This reduces the possibility of cross-contamination. Furthermore, peristaltic pumps can be used to extract minimally-disturbed ground water from any size monitoring location at variable low-flow rates. Because of these features, representative samples are simple to collect, and reliable flow-through cells are simple to establish. The biggest drawback with a peristaltic pump is the maximum achievable pumping depth which is equivalent to the height of water column that can be supported by a perfect vacuum. This effectively limits the use of a peristaltic pump to monitoring locations with groundwater depths of less than approximately 25 feet. Also, off-gasing can occur in the tubing as a result of the reduced pressures and high-rate of cyclical loading. If bubbles are observed in the tubing during purging or sampling, the flow rate of the peristaltic pump must be slowed. If bubbles are still apparent, the tubing should be checked for holes and replaced. The final potential disadvantage with a peristaltic pump is the low flow rate. Although advantageous for sampling, this can be inappropriate during purging or development at locations with large extraction volumes. Puls and Barcelona (1996) show that the use of peristaltic pumps does not compromise sample integrity as long as no bubbles form during sampling. If the ground water is saturated with methane or carbon dioxide, it is practically impossible to collect samples without a gas headspace. Pankow (1986) gives advice on how to correct for this problem.

Positive displacement pumps, also called submersible pumps, include, for example, bladder pumps, Keck®, Grundfos Redi-Flo II®, Bennett® and Enviro-Tech Purger ES® pumps. Each of these pumps operates downhole at depths of up to a few hundred feet and rates of up to several gallons per minute. Therefore, submersible pumps are particularly useful for applications requiring the extraction of large volumes of water or for the extraction of ground water from depths in excess of 25 feet. Because the pumps operate downhole, they require appropriately-sized wells. At a minimum, an inside well diameter of at least 1.5 inches typically is required; however, much larger well diameters can be required depending on the selected pump type, extraction depth, and extraction rate. Because typical submersible pump design results in contact between the ground water and internal as well as external surfaces of the pump, rigorous decontamination and quality assurance procedures must be implemented to avoid cross-contamination if a pump that is not dedicated to the well is used for sampling.

#### **A.4.3.2 Development**

Monitoring wells and points should be developed prior to sampling to remove fine sediments from the portion of the formation adjacent to the screen. Development is not required for grab sampling locations. Because development is intended to enhance ground-water production and quality through the removal of fine sediments in the immediate vicinity of the screen, high flow rates and downhole turbulence are beneficial. This is particularly true for monitoring wells because of the formation disturbance usually associated with installation. Development can be accomplished using

any of the methods discussed in Section A.4.3.1 with selection dependent on well/point dimensions, well/point installation procedures, and hydrogeologic conditions.

Development is accomplished through the removal of water from the well/point in combination with screen/sand pack cleansing through agitation of the downhole ground water. The “agitation” is typically provided by pumping at a high flow rate; surging with the pump, a surge block, or a bailer; and/or pumping along the entire length of the screen. As a rule, the more “agitation” that can be provided, the “better” the development. Typically during development, ground water is extracted until dissolved oxygen, pH, temperature, specific conductivity, and water clarity (turbidity) stabilize. Monitoring well/point development should occur a minimum of 24 hours prior to sampling. Development water must be handled in accordance with the site IDW plan.

It is important to maintain a record of development for each location. The development record should include the following information, at a minimum:

- Monitoring point/well number;
- Date and time of development;
- Development method;
- Monitoring point/well depth;
- Volume of water produced;
- Description of water produced;
- Post-development water level and monitoring point/well depth; and
- Field analytical measurements, including pH, temperature, and specific conductivity.

#### **A.4.3.3 Purging**

Purging consists of the evacuation of water from the monitoring location prior to sampling, so that “fresh” formation water will enter the monitoring location and be available for sampling. Because sampling can occur immediately upon completion of purging, it is best to limit ground-water agitation, and consequently, aeration of the ground water and volatilization of contaminants. Two sources for agitation include the purging device and the cascading of water down the screen as the water level in the well drops. To avoid agitation, a low-disturbance device such as a peristaltic pump or bladder pump is recommended for purging, while equipment such as bailers should be avoided. To avoid aeration, wells or points that were initially screened below the water table should be pumped at a rate which prevents lowering of the water table to below the top of the screen, and if practical, wells or points screened across the water table should be pumped at a rate that lowers the total height of the water column no more than 10 percent of the screened interval. Purging should follow the recommendations of Puls and Barcelona (1996).

Typically, the volume of water contained within the monitoring well/point casing is used to estimate the amount of ground water that should be removed during the purge. As a general rule, three times the calculated volume should be removed from the well/monitoring point; however, this can be reduced to between 1 and 3 volumes for low-producing wells and wells with a very large water column, but a very short screened interval. Purging should continue until parameters such as pH, temperature, specific conductance, dissolved oxygen, and ORP stabilize. Sampling should occur as soon after purging as practical, and definitely within 24 hours. Purge waters must be handled in accordance with the site IDW plan.

If a monitoring well/monitoring point is evacuated to a dry state during purging, the monitoring well/monitoring point should be allowed to recharge, and the sample should be collected as soon as sufficient water is present in the monitoring well or monitoring point to obtain the necessary sample quantity. Sample compositing or sampling over a lengthy period by accumulating small volumes of water at different times to obtain a sample of sufficient volume should be avoided.

It is important to record purge information as a part of the sampling record for each location. At a minimum, the following information pertaining to the purge should be recorded:

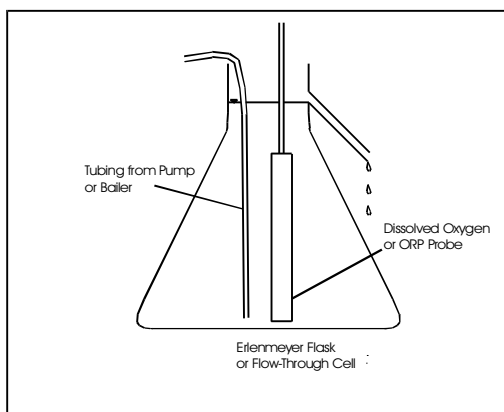
- Monitoring point/well number;
- Date and time of purge;
- Purge method;
- Monitoring point/well depth;
- Volume of water produced;
- Description of water produced;
- Post-purge water level; and
- Field analytical measurements, including pH, temperature, specific conductivity, dissolved oxygen concentration, and ORP;
- Thickness of LNAPL, if present, in the point/well prior to purging;
- Volume of LNAPL removed during purging.

#### **A.4.3.4 Sampling**

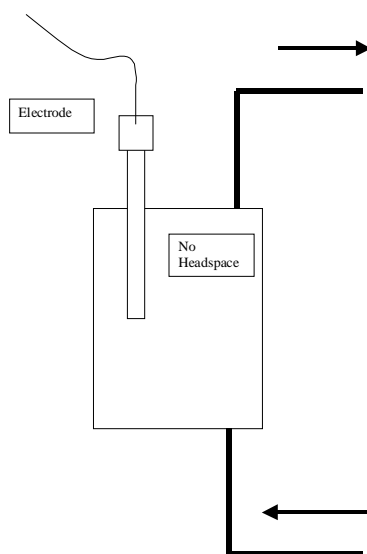
Sampling should occur immediately after purging. If well yield is less than 1/10 of a liter per minute, sample according to the guidance provided by Puls and Barcelona (1996). The object of sampling is the collection of representative ground-water samples. This means that impact to the sample as a result of turbulence, contact with equipment, or a change in conditions must be minimized. The use of a peristaltic pump with dedicated HDPE tubing is recommended for monitoring locations where the depth to water is less than 25 feet because the peristaltic pump is capable of providing a steady, low-flow, stream of ground water which has contacted only dedicated tubing. In addition, conditions are relatively unchanged, so long as care is taken to ensure that the pumping suction does not cause the ground water to boil as a result of the reduced pressure. Where the depth to ground water is greater than 25 feet, a dedicated positive displacement pump, when available, is best. Because of the decontamination difficulties and the resulting potential for cross-contamination associated with most positive displacement pumps, sampling through these pumps is not recommended unless the pumps are dedicated. A bailer should be used only if it is the only means of obtaining a sample.

An overflow cell, such as the one pictured on Figure A.4.1, or a flow-through cell as pictured in Figure A.4.2, should be used for the measurement of well-head parameters, including pH, temperature, specific conductance, dissolved oxygen, and ORP. When using a pump to purge or sample, the pump intake tubing should be positioned near the bottom of the cell. If using a bailer, the water should be drained from the bottom of the bailer through tubing into the cell. In either case, the tubing should be immersed alongside the dissolved oxygen probe beneath the water level in the cell. This will minimize aeration and keep water flowing past the dissolved oxygen probe's sampling membrane. The probes for the other parameters are less sensitive to positioning within the flow-through cell.

Samples should be collected directly from the pump discharge tube or bailer into a sample container of appropriate size, style, and preservation for the desired analysis. Water should be directed down the inner walls of the sample bottle to minimize aeration of the sample. All samples to be analyzed for volatile constituents (e.g., SW8010, SW8020, SW8240, SW8260, and TPH-g) or dissolved gases (e.g., methane, ethane, and ethene) must be filled and sealed so that no air space remains in the container. Sample handling procedures are further described in Section A.6.



**Figure A.4.1** *Overflow cell to prevent alteration of geochemical properties of ground water by exposure to the atmosphere.*



**Figure A.4.2.** *Flow-through cell to prevent alteration of geochemical properties of ground water by exposure to the atmosphere.*

#### A.4.4 GROUND-WATER ANALYTICAL PROCEDURES

In order to demonstrate the efficacy of monitored natural attenuation, field and laboratory analyses should be performed on all ground-water samples using the analytical procedures listed in Table 2.1. As a result of analyte properties and available detection equipment, analyses can be performed at the sampling location, a portable field laboratory, or a fixed-base laboratory. The dissolved hydrogen analysis is unique in that it requires a combination of well-head and field laboratory procedures that are somewhat different from other field methods; therefore, it is presented in a separate subsection. Several of the analytes or parameters can be measured in more than one manner; consequently, the methods provided in this section should not be considered absolute. Rather, these methods have been proven to provide reliable information. The site-specific data quality needs

of each project will be determined during the Data Quality Objective Process and documented in the Quality Assurance Plan.

In order to obtain accurate and defensible data, it is critical that quality assurance procedures are followed for all analyses. These procedures generally fall into the following categories:

- Collection and handling of samples;
- Calibration of direct read meters, chromatographs, colorimeters, and field instruments per manufacturer's instructions;
- Decontamination of equipment and containers; and
- Confirmation of results through analysis of blanks, duplicates, and other quality control samples.

Actual procedures are equipment and analysis specific, and must be developed accordingly.

#### **A.4.4.1 Standard Well-Head Analyses**

Standard well-head analyses include pH, conductivity, temperature, dissolved oxygen, and ORP because these parameters can be measured with a direct-reading meter. This allows all of these parameters to be used as indicators for ground-water stability during development and purging activities. In addition, dissolved oxygen and ORP can be used to provide real time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Temperature, dissolved oxygen, and ORP must be measured at the well head in unfiltered, unpreserved, "fresh" water because these parameters can change significantly within a short time following sample acquisition. Section 2.3.2 of the protocol document describes each analysis and its use in the demonstration of monitored natural attenuation.

It is critical that samples collected for well-head analyses are disturbed and aerated as little as possible; therefore, the use of a flow-through cell, as described in Section A.4.3 and illustrated on Figure A.4.1, is recommended. Where this is not possible, measurements can be made in a clean glass container separate from those intended for laboratory analysis. Where ground-water extraction disturbs the sample, downhole probes can be used for dissolved oxygen analyses, but such probes must be thoroughly decontaminated between wells. In some cases, decontamination procedures can be harmful to the dissolved oxygen probe, and inadequate decontamination can create potential cross-contamination problems if performed prior to sample collection for the other analytes. After sample acquisition, the downhole ground water may be too disturbed to collect an accurate downhole DO measurement.

#### **A.4.4.2 Dissolved Hydrogen Analysis**

As described in Section 2.3.2.9, dissolved hydrogen ( $H_2$ ) concentrations can be an indicator of microbially mediated redox processes in ground-water systems. Determination of  $H_2$  concentrations is a two-step process in the field: sampling at the well head and analysis with a reducing gas detector.

Hydrogen is highly volatile, and this chemical property can be used to measure  $H_2$  concentrations in ground water. The principle is to continuously pump ground water through a gas-sampling bulb containing a nitrogen or air "bubble" so that the  $H_2$  can partition between the gas and liquid phases until the concentration of  $H_2$  in the bubble comes into equilibrium with concentration of  $H_2$  in the ground water. The bubble is then analyzed for  $H_2$  and the concentration of  $H_2$  in the ground water is calculated using the Ideal Gas Law and Henry's Law. This method is referred to as the "bubble strip" method (Chapelle et al., 1995,1997), because the bubble "strips"  $H_2$  out of the water.

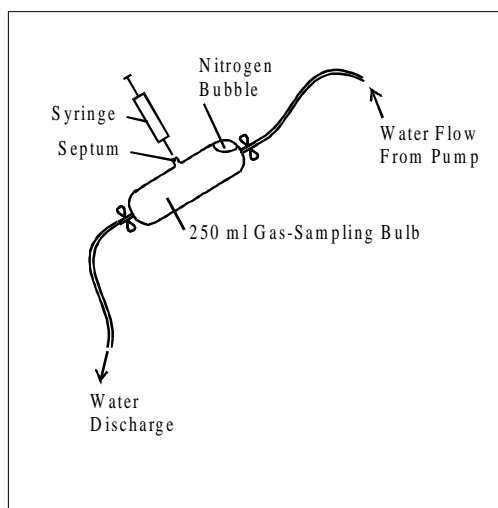
##### **A.4.4.2.1 Sampling Method**

The following procedures are recommended for the collection of a sample for analysis by the "bubble strip" method:

1. Place the intake hose of a peristaltic pump, a Bennett positive displacement pump, or a bladder pump into the sampling well at the depth of the screened interval.

Do not sample for  $H_2$  with electrical submersible pumps because they may produce hydrogen. Do not sample for  $H_2$  from wells with metal screens or casings because they may produce hydrogen and interfere with measurements.

2. Attach a glass, 250-ml gas-sampling bulb (Figure A.4.3) to the outflow end of the tube.
  3. Turn on the pump and adjust the flow rate to between 400 and 700 mL/min.
  4. Briefly hold the outlet end of the sampling bulb in the upright position to remove any gas bubbles from the bulb.
  5. Place the bulb in a horizontal position and inject 20 mL of hydrogen-free  $N_2$  gas through the septum (Figure A.4.3).
  6. Allow the  $N_2$  bubble to come into equilibrium with the flowing ground water for 30 minutes. This equilibration process takes approximately 20 minutes.
  7. Remove 3-5 mL of the gas bubble using a 10 mL glass syringe with attached mini-inert valve.
  8. Close the valve to seal the sample.
  9. Wait an additional 5 minutes and repeat steps 7 and 8.
  10. Analyze both samples on the hydrogen detector, as described in Section A.4.4.2.2.
- Resample the well if the  $H_2$  concentrations of the duplicate samples do not agree within 10 percent.



**Figure A.4.3** Schematic showing the “bubble strip” method for measuring dissolved hydrogen concentrations in ground water.

#### A.4.4.2.2 Analytical Method

Concentrations of  $H_2$  in the nitrogen bubble are determined by gas chromatography (GC) with reduction gas detection (Trace Analytical, Menlo Park, CA). To perform this analysis, a gaseous sample is injected into the stream of a carrier gas such as  $N_2$ . The sample is transported by the carrier through a separation column where the components of the sample are separated on the basis of variations in their transport efficiency through the column matrix. The column is packed with CarboSieve II which separates chemical species primarily on the basis of molecular size. The separated components elute from the column and pass through a heated bed of  $HgO$  where the reduced gases (primarily  $H_2$  and  $CO$ ) are oxidized and  $Hg$  vapor is released. The concentration of  $Hg$  vapor released is directly proportional to the concentration of reduced gases present in the sample and is

detected by means of an ultraviolet photometer. Because chlorinated solvents can destroy the HgO bed, the column is backflushed immediately after the H<sub>2</sub> peak is quantified.

The concentration of H<sub>2</sub> dissolved in the ground water can be calculated from the equilibrated concentration in the nitrogen gas bubble as follows:

- 1) Prepare a calibration curve for H<sub>2</sub> using a 100 ppm Scotty II standard gas mixture. The calibration curve should range from 0.1 to 10.0 µL/L (ppm).
- 2) Analyze the gas sample taken from the gas-sampling bulb, obtaining results (C<sub>B</sub>) in units of µL/L (ppm) in the gas phase.
- 3) Calculate the aqueous concentration of H<sub>2</sub> (C<sub>w</sub> in nanomoles per liter (nM)) in equilibrium with the equilibrated bubble gas (C<sub>B</sub>, µL/L (ppm)) sample using the conversion factor:

$$C_w = 0.81 C_B \quad \text{eq. A.4.1}$$

This conversion factor is derived from the Ideal Gas Law and Henry's Law as follows:

$$PV = nRT \quad (\text{Ideal Gas Law}) \quad \text{eq. A.4.2}$$

Rearrange to give:

$$\frac{n}{V} = \frac{P}{RT} \quad \text{eq. A.4.3}$$

Where:

n = the quantity of gas in moles

V = the volume the gas occupies in Liters

P = the partial pressure of the gas in atm

T = the temperature in °K

R = the gas constant (R = 0.08205 atm L mole<sup>-1</sup> °K<sup>-1</sup>)

Thus the concentration of a pure gas at atmospheric pressure and room temperature is 40.9mmoles/L.

For a 1.0 ppm calibration standard (i.e., 1.0 µL/L), the H<sub>2</sub> concentration in molar units would be:

$$(40.9 \text{mmoles} / L_{H_2})(10^{-6} L_{H_2} / L_{gas})(10^6 \text{nmoles} / \text{mmoles}) = 40.9 \text{nmoles} / L_{gas} \quad \text{eq. A.4.4}$$

The dissolved H<sub>2</sub> concentration in the aqueous phase is given by Henry's Law:

$$C_w = \frac{C_h}{H_{H_2}} \quad \text{eq. A.4.5}$$

$$\text{Conversion factor} = \frac{(40.9 \text{nmoles} L^{-1} \text{ppm}^{-1})}{50.4} = 0.81 \quad \text{eq. A.4.6}$$

Where:

C<sub>w</sub> = the dissolved H<sub>2</sub> concentration in nmoles/L

C<sub>h</sub> = the equilibrated bubble H<sub>2</sub> concentration in nmoles/L

H<sub>H2</sub> = the dimensionless Henry's Law coefficient for the distribution of H<sub>2</sub> between the gaseous and dissolved phases (H<sub>H2</sub> = 50.4).

- 4) Identify the predominant terminal electron accepting process for the water sample using the characteristic ranges presented in Table 2.5.

#### A.4.4.3 Field Analytical Laboratory Analyses

The field analytical laboratory analyses to be used for ground-water samples are presented in Table 2.1. These analyses include parameters that are time-sensitive or can be performed accurately, easily, and inexpensively on site. In addition, results obtained from field laboratory analyses provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. This real-time data can be used to guide the investigation of monitored natural

attenuation at sites with limited or ambiguous hydrogeologic and plume information. Section 2.3.2 of the protocol document describes each analysis and its use in the demonstration of monitored natural attenuation.

In preparation for field laboratory analysis, all glassware or plasticware used in the analyses must be cleaned thoroughly by washing with a solution of laboratory-grade, phosphate-free detergent (such as Alconox®) and water, and rinsing with deionized water and ethanol to prevent interference or cross-contamination between measurements. If concentrations of an analyte are above the range detectable by the titrimetric method, the analysis should be repeated by diluting the ground-water sample with double-distilled water until the analyte concentration falls to a level within the range of the method. All rinseate and sample reagents accumulated during ground-water analysis must be handled appropriately, including collection, labeling, storage, and disposal.

Carbon dioxide (CO<sub>2</sub>) is a byproduct of naturally occurring aerobic and anaerobic biodegradation processes that occur in ground water. Carbon dioxide concentrations in ground water can be measured in the field by titrimetric analysis using CHEMetrics® Method 4500 (0 to 250 mg/L as CO<sub>2</sub>), or similar.

An increase in the alkalinity of ground water above background may be produced when carbon dioxide produced by biological activity reacts with carbonate minerals in the aquifer matrix material. Alkalinity of the ground-water sample will be measured in the field by titrimetric analysis using U.S. EPA-approved Hach® Method 8221 (0 to 5,000 mg/L as calcium carbonate), or similar.

Nitrate-nitrogen concentrations are of interest because nitrate can act as an electron acceptor during hydrocarbon biodegradation under anaerobic soil or ground-water conditions. Nitrate-nitrogen is also a potential nitrogen source for hydrocarbon-degrading bacteria biomass formation. Nitrite-nitrogen is an intermediate byproduct in both ammonia nitrification and in nitrate reduction in anaerobic environments. Nitrate- and nitrite-nitrogen concentrations in ground water can be measured in the field by colorimetric analysis using a portable colorimeter (such as the Hach® DR/700). Nitrate concentrations in ground-water samples can be analyzed after preparation with Hach® Method 8039 (0 to 30.0 mg/L nitrate), or similar. Nitrite concentrations in ground-water samples can be analyzed after preparation with U.S. EPA-approved Hach® Method 8507 (0 to 0.35 mg/L nitrite), or similar.

Sulfate in ground water is a potential electron acceptor for fuel-hydrocarbon biodegradation in anaerobic environments, and sulfide is produced by biological sulfate reduction. Sulfate and sulfide concentrations can be measured by colorimetric analysis with a portable colorimeter (such as the Hach® DR/700) after appropriate sample preparation. U.S. EPA-approved Hach® Methods 8051 (0 to 70.0 mg/L sulfate) and 8131 (0.60 mg/L sulfide) (or similar) can be used to prepare samples and analyze sulfate and sulfide concentrations, respectively.

Iron III is an electron acceptor for biological metabolism under anaerobic conditions. Iron III is the substrate for biological iron reduction; Iron II is the product. Iron concentrations can be measured in the field by colorimetric analysis with a portable colorimeter (such as a Hach® DR/700) after appropriate sample preparation. Hach® Method 8008 for total soluble iron (0 to 3.0 mg/L ferric + ferrous iron) and Hach® Method 8146 for ferrous iron (0 to 3.0 mg/L) (or similar) can be used to prepare and quantitate the samples. Ferric iron is quantitated by subtracting ferrous iron levels from total iron levels.

Manganese is a potential electron acceptor under anaerobic environments. Manganese concentrations can be quantitated in the field using colorimetric analysis with a portable colorimeter (such as a Hach® DR/700). U.S. EPA-approved Hach® Method 8034 (0 to 20.0 mg/L), or similar, can be used to prepare the samples for quantitation of manganese concentrations.

#### **A.4.4.4 Fixed-Base Laboratory Analyses**

The fixed-base laboratory analyses to be used for ground-water samples are presented in Table 2.1. These analyses include the parameters that cannot be easily or accurately performed in the field, but are necessary to document monitored natural attenuation of fuel hydrocarbons and chlorinated solvents in ground water. Section 2.3.2 of the protocol document describes each analysis and its use in the demonstration of monitored natural attenuation.

Prior to sampling, arrangements should be made with the analytical laboratory (or other supplier) to provide a sufficient number of appropriate sample containers for the samples (including quality control samples) to be collected. All containers, preservatives, and shipping requirements should be consistent with the analytical protocol. For samples requiring chemical preservation, preservatives are best added to containers by the laboratory (or other supplier) prior to shipping. Sample handling is discussed in Section A.6.

## **SECTION A-5**

### **SURFACE WATER AND SEDIMENT CHARACTERIZATION METHODOLOGIES**

At sites where surface water bodies are affected (or potentially affected) by contamination, surface water and sediment sample collection and analysis may be required as a component of the remediation by monitored natural attenuation demonstration.

#### **A.5.1 SURFACE WATER SAMPLE COLLECTION**

Surface water can be collected with a peristaltic pump using exactly the same equipment and procedures to collect water from a well. The sampling tube can be introduced into the water from a barge or boat, or from a dock. The depth to the sediment should be sounded, then the tube introduced to a level a very few inches above the sediment layer. A weight can be used to keep the tube straight. Alternately, ½ inch PVC pipe can be inserted to the correct depth, then sampled with a tube just as if it were a well.

Many plumes discharge at some distance away from the shoreline of lakes or large rivers. Samples should be taken at locations where the elevation of the sediment-to-water interface corresponds to the elevation of the contaminant plume in the aquifer. Many plumes are driven down into aquifers by recharge. Conversely, the flow path bends sharply up underneath a gaining stream at the point of discharge. Water just above the sediment in the center of a stream or small river should be sampled. If possible, the stage of a stream or river at a gauging station near the point of sampling should be determined to estimate the discharge of the stream or river at the time of sampling. Losing streams or rivers should not be sampled at high stage when they are losing water because groundwater plumes would be pushed away from the sediment interface. To ensure that the stream is not losing, the elevation of standing water in monitoring wells near the river should be higher than the stage of the river or stream at the time of sampling. The same considerations apply to tidal environments or areas with wind seiches on large bodies of water. Surface water should be sampled when the tide is out, or the wind is blowing off-shore. Additionally, contaminant plumes may be deflected strongly downstream by flow occurring within the saturated material surrounding the surface water channel. This is particularly true when the hydraulic conductivity of the stream sediments is much greater than the hydraulic conductivity of the surrounding material that supplies ground water to the stream. A great deal of thought as to when and where to sample is necessary to yield meaningful results.

#### **A.5.2 SEDIMENT SAMPLE COLLECTION**

Sediment samples below the water surface can be collected using a core barrel. The core barrel can be hand driven to the desired depth from a boat, then pulled back up using a mechanical jack after sampling is finished. An alternative technique is to place open-end, two-inch diameter PVC tubing to a desired depth, then insert flexible tubing and collect the sediment as a slurry into a suction flask connected to a peristaltic pump.

## **SECTION A-6**

### **SAMPLE HANDLING**

This section describes the handling of soil and ground-water samples from the time of sampling until the samples arrive at the laboratory.

#### **A.6.1 SAMPLE PRESERVATION, CONTAINERS, AND LABELS**

Sample containers and appropriate container lids must be purchased or provided by the analytical laboratory. Any required chemical preservatives can be added to the sample containers by the analytical laboratory prior to shipping the containers to the site or alternatively, at the time of sampling. The sample containers should be filled and tightly sealed in accordance with accepted procedures for the sample matrix and the type of analysis to be conducted. The sample label should be firmly attached to the container side, and the following information legibly and indelibly written on the label:

- Facility name;
- Sample identification;
- Sample type (groundwater, surface water, etc.);
- Sampling date;
- Sampling time;
- Preservatives added; and
- Sample collector's initials.

#### **A.6.2 SAMPLE SHIPMENT**

After the samples are sealed and labeled, they should be packaged for transport to the analytical laboratory. The packaged samples should be delivered to the analytical laboratory shortly after sample acquisition using an overnight delivery service. The following packaging and labeling procedures are to be followed:

- Abide by all U.S. Department of Transportation (DOT) shipping regulations;
- Package samples so that they will not leak, spill, or vaporize from their containers;
- Place samples in a cooler containing ice to maintain a shipping temperature of approximately 4 degrees centigrade (°C), if required by the requested analyses;
- Include a properly completed chain-of-custody form, as described in the following subsection; and
- Label shipping container with
  - Sample collector's name, address, and telephone number;
  - Laboratory's name, address, and telephone number;
  - Description of sample;
  - Quantity of sample; and
  - Date of shipment.

#### **A.6.3 CHAIN-OF-CUSTODY CONTROL**

After the samples are collected, chain-of-custody procedures must be followed to establish a written record of sample handling and movement between the sampling site and the analytical laboratory. Each shipping container should include a chain-of-custody form completed in triplicate by the sampling personnel. One copy of this form should be kept by the sampling contractor after sample delivery to the analytical laboratory; the other two copies should be retained at the laboratory. One of the laboratory copies will become a part of the permanent record for the sample and will be returned with the sample analytical results. The chain-of-custody form should contain the following information:

- Unique sample identification number;
- Sample collector's printed name and signature;
- Date and time of collection;
- Sample location;
- Sample matrix;
- Sample size and container;
- Chemical preservatives added;
- Analyses requested;
- Signatures of individuals involved in the chain of possession; and
- Inclusive dates of possession.

The chain-of-custody documentation should be placed inside the shipping container so that it will be immediately apparent to the laboratory personnel receiving the container, but cannot be damaged or lost during transport. The shipping container is to be sealed so that it will be obvious if the seal has been tampered with or broken.

#### **A.6.4 SAMPLING RECORDS**

In order to provide complete documentation of the sampling event, detailed records must be maintained by the field scientist. At a minimum, these records must include the following information:

- Sample location (facility name);
- Sample identification;
- Sample location map or detailed sketch;
- Date and time of sampling;
- Sampling method;
- Field observations of
  - Sample appearance,
  - Sample odor;
- Weather conditions;
- Water level prior to purging (ground-water samples);
- Total well depth (ground-water samples);
- Purge volume (ground-water samples);
- Water level after purging (ground-water samples);
- Well condition (ground-water samples);
- Sample depth;
- Sampler's identification;
- Field measurements such as pH, temperature, specific conductivity, dissolved oxygen concentration, and redox potential (ground-water samples); and
- Any other relevant information.

## **SECTION A-7**

### **AQUIFER CHARACTERIZATION METHODOLOGIES**

Adequate characterization of the ground-water flow and contaminant transport system is an important component of the monitored natural attenuation demonstration. The following sections describe methodologies that are recommended to characterize the hydrogeologic system.

#### **A.7.1 HYDRAULIC CONDUCTIVITY**

Hydraulic conductivity is a measure of an aquifer's capacity to transmit water and governs ground-water flow and contaminant transport in the subsurface. Methods for determining hydraulic conductivity in the field can include slug tests, pumping tests, and downhole flowmeter measurements. Hydraulic conductivity can also be measured during penetration with a cone penetrometer by measuring the transient pressure excursions in the pore water in front of the cone using a cone equipped with a pressure transducer in contact with the pore water. The method selected for a given site will depend on the dimensions, locations, and screened intervals of site wells and monitoring points; site stratigraphy; equipment availability; budget; and waste handling requirements.

##### **A.7.1.1 Pump Tests**

A pumping test involves pumping one well at a constant rate for a specified length of time and collecting periodic water level measurements in both the pumped well and nearby observation wells in order to determine aquifer hydraulic characteristics representative of a large area. As a rule, pumping tests provide more representative measurements of hydraulic parameters; however, they require a greater commitment of resources (time, money, and equipment) that cannot be afforded by all projects. In addition, for pumping test results to be representative, site hydrogeologic conditions should not change appreciably over short distances. This section outlines methods that can be used for conducting pump tests in both confined and unconfined aquifers. For a more detailed discussion of how to conduct a pumping test, the reader is referred to the work of Dawson and Istok (1991), Kruseman and de Ridder (1991), and Driscoll (1986).

The interpretation of aquifer pumping test data is not unique. Similar sets of data can be obtained from various combinations of geologic conditions. The interpretation of pumping test data is discussed in Appendix C of this protocol document.

##### **A.7.1.1.1 Pumping Test Design**

Prior to performing an aquifer pumping test, all available site and regional hydrogeologic information should be assembled and evaluated. Such data should include ground-water flow direction, hydraulic gradients, other geohydraulic properties, site stratigraphy, well construction details, regional water level trends, and the performance of other pumping wells in the vicinity of the test area. This information is used to select test duration, proposed pumping rates, and pumping well and equipment dimensions.

The precise location of an aquifer test is chosen to be representative of the area under study. In addition, the location is selected on the basis of numerous other criteria, including:

- Size of the investigation area;
- Uniformity and homogeneity of the aquifer;
- Distribution of contaminant sources and dissolved contaminant plumes;
- Location of known or suspected recharge or barrier boundary conditions;
- Availability of pumping and/or observation wells of appropriate dimension and screened at the desired depth; and
- Requirements for handling discharge.

The dimensions and screened interval of the pumping well must be appropriate for the tested aquifer. For example, the diameter of the well must be sufficient to accommodate pumping equip-

ment capable of sustaining the desired flow rate at the given water depth. In addition, if testing a confined aquifer that is relatively thin, the pumping well should be screened for the entire thickness of the aquifer. For an unconfined aquifer, the wells should be screened in the bottom one-third or two-thirds of the saturated zone.

Any number of observation wells may be used. The number chosen is contingent upon both cost and the need to obtain the maximum amount of accurate and reliable data. If three or more observation wells are to be installed, and there is a known boundary condition, the wells should be placed along a radial line extending from the pumping well toward the boundary, with one well placed perpendicular to the line of observation wells to determine whether radial anisotropy exists within the aquifer. If two observation wells are to be installed, they should be placed in a triangular pattern, non-equidistant from the pumping well. Observation wells should be located at distances and depths appropriate for the planned method for analysis of the aquifer test data. Observation well spacing should be determined based upon expected drawdown conditions that are the result of the studies of geohydraulic properties, proposed pumping test duration, and proposed pumping rate. Preliminary pumping results should also be used (if available). Not all projects can afford the luxury of preliminary testing.

The equipment needed to perform aquifer pumping tests includes:

- |  |  |
|--|--|
| • Pumps                                  | • Conductivity meter, pH meter, and thermometer        |
| • Gate valve                             | • Barometer  |
| • Electrical generator                   | • Semi-log and log-log graph paper                     |
| • Flow meter with totalizer              | • Portable computer                                    |
| • Water level indicators                 | • Field printer for data                               |
| • Pressure gauge                         | • Type matching curves                                 |
| • Field logbook/forms                    | • Meter and stopwatch for discharge measurement        |
| • Pressure transducers and data recorder | • Hose or pipe for transfer of water                   |
| • Engineer's tape calibrated to 0.01 ft  | • Adequately sized tank for storing contaminated water |
| • 5-gallon pail                          |  |

Pumping equipment should conform to the size of the well and be capable of delivering the estimated range of pumping rates. The selection of flow meter, gate valve, and water transfer lines should be based on anticipated rates of water discharge. Both the discharge rate and test duration should be considered when selecting a tank for storing discharge water if the water cannot be released directly to the ground, sanitary sewer, storm sewer, or nearby water treatment facility.

In areas of severe winter climates, where the frost line may extend to depths of several feet, pumping tests should be avoided during cold weather months where the water table is less than 12 feet from the surface. Under certain conditions, the frozen soil acts as a confining stratum, and combined with leaky aquifer and delayed storage characteristics, test results may be unreliable.

#### A.7.1.1.2 Preparation for Testing

Barometric changes may affect water levels in wells, particularly in semiconfined and confined aquifers. A change in barometric pressure may cause a change in the water level. Therefore, for at least 24 hours prior to performing a pumping test, barometric pressure and water levels in the test well, observation wells, and a well beyond the influence of the pumping well should be measured hourly to establish trends in ground-water level fluctuation. If a trend is apparent, the barometric pressure should be used to develop curves depicting the change in water level versus time. These curves should be used to correct the water levels observed during the pumping test. Ground-water levels in the background well as well as barometric pressures should continue to be recorded throughout the duration of the test.

Test wells should undergo preliminary pumping or step drawdown tests prior to the actual test. This will enable fines to be flushed from the adjacent formation near the well and a steady flow rate to be established. The preliminary pumping should determine the maximum drawdown in the well and the proper pumping rate should be determined by step drawdown testing. The aquifer should then be given time to recover before the actual pumping test begins (as a rule-of-thumb, one day).

A record should be maintained in the field logbook of the times of pumping and discharge of other wells in the area, and if their radii of influence intersect the cone of depression of the test well. All measurements and observations should be recorded in a field notebook or on an Aquifer Test Data Form. If data loggers with transducers are used, field measurements should be performed in case of data logger malfunction.

#### **A.7.1.1.3 Conducting the Pumping Test**

Immediately prior to starting the pump, the water levels should be measured and recorded for all wells to determine the static water levels upon which all drawdowns will be based. Data loggers should be reset for each well to a starting water level of 0.0 foot.

Water pumped from an unconfined aquifer during a pumping test should be disposed of in such a manner as not to allow the aquifer to be recharged by infiltration during the test. This means that the water must be piped away from the well and associated observation wells. Recharge could adversely affect the results. Also, if contaminated water is pumped during the test, the water must be stored and treated or disposed of according to the project work plan for the study. The discharge water may be temporarily stored in drums, a lined, bermed area, or tanks. If necessary, it should be transported and staged in a designated secure area.

The discharge rate should be measured frequently throughout the test and controlled to maintain it as constant as possible, after the initial excess discharge has been stabilized. This can be achieved by using a control valve.

The pitch or rhythm of the pump or generators provides a check on performance. If there is a sudden change in pitch, the discharge should be checked immediately and proper adjustments to the control valve or the engine speed should be made, if necessary. Do not allow the pump to break suction during the test. Allow for maximum drawdown of the well during the step drawdown test. If done properly, the flow control valve can be pre-set for the test and will not have to be adjusted during pumping. If the pump does shut down during the test, make necessary adjustments and restart the test after the well has stabilized. For a confined aquifer, the water level in the pumping well should not be allowed, if possible, to fall below the bottom of the upper confining stratum during a pumping test.

At least 10 measurements of drawdown for each log cycle of time should be made both in the test well and the observation wells. Data loggers can be set to record in log time, which is very useful for data analysis. A suggested schedule for recording water level measurements made by hand is as follows:

- 0 to 10 minutes - 0.5, 1.0, 2.5, 2.0, 2.5, 3.0, 4.5, 6.5, 8, and 10 minutes. It is important in the early part of the test to record with maximum accuracy the time at which readings are taken.
- 10 to 100 minutes - 10, 15, 20, 25, 30, 40, 50, 65, 80, and 100 minutes.
- Then, at 1-hour intervals from 120 minutes to 1,440 minutes (one day) and every 2 hours after 1 complete day.

Initially, there should be sufficient field personnel to station one person at each well used in the pumping test (unless an automatic water-level recording system has been installed). After the first two hours of pumping, two people are usually sufficient to complete the test. A third person may be needed when treatment of the pumped water is required prior to discharge. It is advisable for at least

one field member to have experience in the performance of pump tests, and for all field personnel to have a basic familiarity with conducting the test and gathering data.

Field personnel should be aware that electronic equipment sometimes fails in the field. Some field crews have experienced complete loss of data due to failure of a logger or transducer. It is a good idea to record data in the field logbook or on a manual form as the data are produced. That way, the data are not lost should the equipment fail.

The discharge or pumping rate should be measured with a flow meter that also has a totalizer. When the pumping is complete, the total gallons pumped are divided by the time of pumping to obtain the average discharge rate for the test. Periodic checking and recording of the pumping rate during the test also should be performed.

The total pumping time for a test depends on the type of aquifer and degree of accuracy desired. Economizing on the duration of pumping is not recommended. More reliable results are obtained if pumping continues until the cone of depression achieves a stabilized condition. The cone of depression will continue to expand at an ever-decreasing rate until recharge of the aquifer equals the pumping rate, and a steady-state condition is established. The time required for steady-state flow to occur may vary from a few hours to years.

Under normal conditions, it is a good practice to continue a pumping test in a confined aquifer for at least 24 hours, and in an unconfined aquifer for a minimum of 72 hours. A longer duration of pumping may reveal the presence of boundary conditions or delayed yield. Use of portable computers allows time/drawdown plots to be made in the field. If data loggers are used to monitor water levels, hard copies of the data printed on field printers should be obtained before transporting the logger back to the office for downloading.

#### **A.7.1.2 Slug Tests**

A slug test is a single-well hydraulic test used to determine the hydraulic conductivity of an aquifer in the immediate vicinity of the well. Because hydraulic conductivity varies spatially within and between aquifers and because slug test results reflect aquifer conditions only in the immediate vicinity of the tested well, slug tests should be conducted in as many wells as possible at a site. Slug tests can be used for both confined and unconfined aquifers that have transmissivities of less than approximately 7,000 square feet per day (ft<sup>2</sup>/day). Slug tests are accomplished by removing a solid slug (rising head) or introducing a solid slug (falling head), and then allowing the water level to stabilize while taking water level measurements at closely spaced time intervals. The method presented herein discusses the use of falling head and rising head slug tests in sequence. The analysis of slug test data is discussed in Appendix C.

Slug testing should not proceed until water level measurements show that static water level equilibrium has been achieved. Unvented wells should be uncapped at least 24 hours prior to initiating the test in order to allow the static water level to come to equilibrium. The protective casing should remain locked during this time to prevent vandalism. During the slug test, the water level change should be influenced only by the introduction or removal of the slug volume. Other factors, such as inadequate well development or extended pumping, may lead to inaccurate results. It is the field scientist's responsibility to decide when static equilibrium has been reached in the well.

The following equipment is needed to conduct a slug test:

- Teflon<sup>®</sup>, PVC, or metal slug
- Nylon or polypropylene rope
- Electric water level indicator
- Pressure transducer/sensor
- Field logbook/forms
- Automatic data recorder (such as the Hermit Environmental Data Logger<sup>®</sup>, In-Situ, Inc. Model SE1000B, or equal)

The falling head test is the first step in the two-step slug-testing procedure. The following steps describe the recommended falling head slug test procedure:

1. Decontaminate all downhole equipment.
2. Record pre-test information including: well number, personnel, climatic data, ground surface elevation, measuring point elevation, equipment identifications, and date.
3. Measure and record the static water level in the well to the nearest 0.01 foot.
4. Lower the decontaminated pressure transducer into the well and allow the displaced water to return to within 0.01 foot of the original static level.
5. Lower the decontaminated slug into the well to just above the water surface in the well.
6. Start the data logger and quickly lower the slug below the water table being careful not to disturb the pressure transducer. Follow the owner's manual for proper operation of the data logger.
7. Terminate data recording when the water level has recovered at least 80 percent from the initial slug displacement.

Immediately following completion of the falling head test, the rising head test is performed.

The following steps describe the rising head slug test procedure:

1. Measure the static water level in the well to the nearest 0.01 foot to ensure that it has returned to the static water level.
2. Initiate data recording and quickly withdraw the slug from the well. Follow the owner's manual for proper operation of the data logger.
3. Terminate data recording when the water level has recovered at least 80 percent from the initial slug displacement.

It is advisable to produce hard copies or backup electronic copies of the data logger output (draw-down vs. time) daily and before transporting the logger from the field site.

#### **A.7.1.3 Downhole Flow Meter Measurements**

Downhole flow meter measurements are used to investigate the relative vertical distribution of horizontal hydraulic conductivity in an open borehole or the screened portion of a well. These measurements are useful for identifying zones of elevated hydraulic conductivity that may contribute to preferential flow pathways and affect contaminant migration. Methodologies for interpreting data from borehole surveys are described by Molz *et al.* (1994).

Flowmeter measurements should be performed at 1- to 3-foot intervals in test wells during both ambient conditions and induced flow conditions. Test data may be analyzed using the methods described by Molz *et al.* (1994) to define the relative distribution of horizontal hydraulic conductivity within the screened interval of each well. Final results should be presented in tabular and graphical forms and accompanied by appropriate interpretation and discussion. Estimates of bulk hydraulic conductivity from previous aquifer tests or results of single-well tests conducted in conjunction with the flow meter survey can be used to estimate the absolute hydraulic conductivity distribution at each well.

Borehole flowmeters should be calibrated prior to testing. Generally, 0.5-inch-ID and 1.0-inch-ID probes will be calibrated using a range of volumetric flowrates potentially applicable to most sites [e.g., approximately 0.04 liters per minute (L/min) to 10 L/min]. The following nine steps outline general procedures that can be used to conduct a downhole flow meter survey at a given location.

- Measure the water level, organic liquid (NAPL) interfaces (if present), and total depth (TD) prior to initiating the test.
- Calibrate the flow meter for the range of anticipated flow velocities before introducing the flow meter into the well or borehole.
- Lower the flow meter to the bottom of the well/borehole.

- Slowly withdraw the flow meter, pausing to obtain measurements at intervals of approximately 1 to 3 feet, depending on site conditions. This will provide a baseline under static (ambient) conditions.
- Conduct a short-term, single-well pumping test in the test well to stress the aquifer.
- Record drawdown using an electronic data logger with a pressure transducer.
- Monitor and adjust the ground-water extraction rate, as necessary, to maintain constant flow.
- Obtain the profile of the vertical flow at the same elevations occupied during the ambient profile upon stabilization of the flow rate.
- Analyze the data collected during the tests to estimate relative distribution of flow into the tested wells and the relative hydraulic conductivity distribution at each location (Molz *et al.*, 1994).

### **A.7.2 HYDRAULIC GRADIENT**

Hydraulic gradient, defined as the change in ground-water elevation with distance, is a key parameter governing the direction and rate of ground-water flow and contaminant migration. Because ground water can flow in both the horizontal and vertical planes, both horizontal and vertical gradients are required for a successful demonstration of monitored natural attenuation. Hydraulic gradients are generally calculated on the basis of ground-water elevations measured in site monitoring wells or monitoring points using an electric water level indicator. Therefore, for the most complete representation of site hydrogeology, it is important to measure ground-water elevations from as many depths and locations as available. Interpretation of ground-water elevations and the subsequent calculations for hydraulic gradient are discussed in Appendix C.

### **A.7.3 DIRECT MEASUREMENT OF GROUND-WATER VELOCITY**

Ground-water velocity is directly related to contaminant velocity; therefore, a determination of groundwater velocity is critical to the fate and transport portion of a demonstration of monitored natural attenuation. Typically, ground-water velocity is estimated from the hydraulic conductivity, hydraulic gradient, and effective porosity as described in Appendix C; however, direct measurement of ground-water velocity can be obtained from dye tracer studies.